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(54) **Process for preparing coated carrier particles for electrostatographic developers.**

(57) Electrostatographic conductive coated carrier particles for use in the development of electrostatic latent images are provided by preparing a fluid mixture of insulating resinous material and an electrically conductive agent, converting the fluid mixture to a solid state, and comminuting the solid mixture to dry, powdered particles having a particle size of 1 to 100 microns. The powdered particles are mechanically or electrostatically applied to the surface of carrier cores having a particle size of 30 to 1000 microns. The resultant aggregation is heated to melt and fuse the powdered particles to the surface of the carrier cores. The conductive carrier particles are mixed with finely-divided toner particles to form developer mixtures.

EP 0 020 181 A1

PROCESS FOR PREPARING COATED CARRIER PARTICLES FOR ELECTROSTATOGRAPHIC DEVELOPERS

This invention relates to a process for preparing coated carrier particles for electrostatographic developers.

It is well known to form and develop images on the surface of photoconductive materials by electrostatic methods such as described, for example, in U.S. Patents 2,297,691; 2,277,013; 2,551,582; 3,220,324; and 3,220,833. In summary, these processes as described in the aforementioned patents involve the formation of an electrostatic latent charge image on an insulating electrophotographic element and rendering the latent image visible by a development step whereby the charged surface of the photoconductive element is brought into contact with a developer mixture. As described in U.S. Patent 2,297,691, for example, the resulting electrostatic latent image is developed by depositing thereon a finely-divided electroscopic material referred to in the art as toner, the toner being generally attracted to the areas of the layer which retain a charge thus forming a toner image corresponding to the electrostatic latent image. Subsequently, the toner image can be transferred to a support surface such as paper and this transferred image can be permanently affixed to the support surface using a variety of techniques including pressure fixing, heat fixing, solvent fixing, and the like.

Many methods are known for applying the electroscopic particles to the latent image including cascade development, touchdown and magnetic brush as illustrated in U.S. Patents 2,618,552; 2,895,847 and 3,245,823. One of the most widely used methods is cascade development wherein the developer material comprising relatively large carrier particles having finely-divided toner particles electrostatically clinging to the surface of the carrier particles is conveyed to and rolled or cascaded across the electrostatic latent image-bearing surface. Magnetic brush development is also known and involves the use of a developer material comprising toner and magnetic carrier particles which are carried by a magnet so that the magnetic field produced by the magnet causes alignment of the magnetic carriers in a brush-like configuration. Subsequently, this brush is brought into contact with the electrostatic latent image-bearing surface causing the toner particles to be attracted from the brush to the electrostatic latent image by electrostatic attraction, as more specifically disclosed in U.S. Patent 2,874,063.

Carrier materials used in the development of electrostatic latent images are described in many patents including, for example, U.S. Patent 3,590,000. The type of carrier material to be used depends on many factors such as the type of development used, the quality of the development desired, the type of photoconductive material employed and the like. Generally, however, the materials used as carrier surfaces or carrier particles or the coating thereon should have a triboelectric value commensurate with the triboelectric value of the toner in order to generate electrostatic adhesion of the toner to the carrier. Carriers should be selected that are not brittle so as to cause flaking of the surface or particle break-up under the forces exerted on the carrier during recycle as such causes undesirable effects and could, for example, be transferred to the copy surface thereby reducing the quality of the final image.

There have been recent efforts to develop carriers and particularly coatings for carrier particles in order to obtain better development quality and also to obtain a material that can be recycled and does not cause any adverse effects to the photoconductor. Some of the coatings commercially utilized deteriorate rapidly especially when employed in a continuous process whereby the entire coating may separate from the carrier core in the form of chips or flakes as a result of poorly adhering coated material and fail upon impact and abrasive contact with machine parts and other carrier particles. Such carrier particles generally cannot be reclaimed and reused and usually provide poor print quality results. Further, the triboelectric values of some carrier coatings have been found to fluctuate when changes in relative humidity occur and thus these carriers are not desirable for use in electrostatographic systems as they can adversely affect the quality of the developed image.

The coating materials employed for carrier particles are generally resins having electrically insulating properties and are usually applied by solution or spray-drying techniques. However, it has been found that when attempts are made to apply an insulating resin coating to porous carrier core materials by solution-coating techniques that the products obtained are undesirable. This is so because most of the coating material is found to reside in the pores of the carrier cores and not at the surface thereof so as to be available for triboelectric charging when the coated carrier particles are mixed with finely-divided toner particles. Attempts to resolve this problem by increasing carrier coating weights, for example, to as much as up to about 3

percent or greater to provide an effective triboelectric charging coating to the carrier particles necessarily involves handling excessive quantities of solvents and usually results in low product yields. It has also been found that toner impaction, i.e., where toner particles become welded to or impacted upon the carrier particles, remains high with thus coated carrier particles producing short developer useful lifetimes. Further, solution-coated porous carrier particles when combined and mixed with finely-divided toner particles provide triboelectric charging levels which are too low for practical use. In addition, solution-coated metallic carrier particles have a high incidence of electrical breakdown at low applied voltages leading to shorting between the carrier particles and the photoreceptor.

Further, when attempting to provide carrier materials having conductive properties such as by partially coating conductive carrier cores with an electrically insulating resin, the amount of coating material applied must be carefully controlled so that enough uncoated areas remain on the carrier cores to provide conductive paths between the carrier material and the photoreceptor. Such partially coated carrier materials are extremely difficult to reproducibly control and manufacture, they produce bimodal triboelectric charging sites, and they have narrow toner concentration latitudes quickly yielding insulating developers and short developer life.

Further, in particular electrostatographic reproduction systems, in order to develop a latent image comprised of negative electrostatic charges, an electrostatic carrier and toner powder combination must be selected in which the toner is triboelectrically charged positively relative to the granular carrier. Likewise, in order to develop a latent image comprised of positive electrostatic charges such as where a selenium photoreceptor is employed, an electroscopic toner powder and carrier mixture must be selected in which the toner is triboelectrically charged negatively relative to the carrier. Thus, where the latent image is formed of negative electrostatic charges such as when employing an organic electrophotosensitive material as the photoreceptor, it is highly desirable to develop the latent image with a positively charged electroscopic powder and a negatively charged carrier material. Thus, there is a continuing need for a better electrostatographic carrier material and an improved method for its preparation.

The present invention is intended to provide a carrier manufacturing technique which results in a product that overcomes the above-noted deficiencies of conventional developer materials.

The process of the invention is characterised by preparing a fluid mixture of insulating resinous material and at least one electrically conductive agent, converting said fluid mixture to a solid state, comminuting said mixture in said solid state to dry, powdered particles, applying said powdered particles to the surface of carrier cores, and heating the resultant aggregation so that said powdered particles fuse to said carrier cores.

The resultant carrier beads have conductive characteristics, greatly increased useful life, and substantially eliminate photoreceptor shorting problems. In addition, the triboelectric values of a carrier material are altered without markedly changing the physical and chemical properties of the original carrier material. Further, the improved developer materials may be used in electrostatographic development environments where the photoreceptor is negatively charged.

The foregoing inventive features are accomplished, generally speaking, by providing coated carrier particles having electrically conductive properties. More specifically, the carrier particles of this invention comprise a core particle having an average diameter of between 30 and 1,000 microns coated with between 0.05 and 3.0 percent by weight, based on the weight of the coated carrier particles, of a mixture of thermoplastic insulating resinous material and at least one agent possessing electrically conductive properties. Generally speaking, the coated carrier particles of this invention are provided by preparing a fluid mixture of thermoplastic insulating resinous material and at least one electrically conductive agent, applying said mixture in the form of dry, powdered particles having a particle size of between 1 and 100 microns to the aforementioned carrier core, and then heating the resultant aggregation to a temperature of between 126°C and 345°C for between 15 and 120 minutes so that the mixture of thermoplastic insulating resinous material and electrically conductive agent fuse to the carrier core particle.

In the initial step of preparing the compositions of this invention, any suitable means may be employed to produce the conductive material-powdered resin mixture. Thus, for example, an insulating resinous material is heat-melted or dissolved in a suitable solvent to bring the resinous material to a fluid or tacky state. To the fluid or tacky resinous composition is added a suitable amount of conductive material and mixed therewith until a uniform mixture is obtained. The resultant resinous composition and conductive

material mixture is then processed to provide dry, powdered particles having a particle size of between about 1 micron and about 100 microns, preferably between 1 micron and about 50 microns. Some of the means which may be employed to provide these dry, powdered resin-conductive material particles include spray-drying the foregoing fluid or tacky mixture or a dispersion thereof, precipitation of a resin-conductive material dispersion, freeze-drying a resin-conductive material dispersion, air or fluid attrition of a resin-conductive material dispersion, direct polymerization such as emulsion polymerization of conductive material in a monomer followed by crushing, grinding, or milling and any other suitable means to obtain the aforedescribed particles.

Following preparation of the dry, powdered resin-conductive material particles described above, the powdered particles are applied to the surface of a carrier core material by, for example, dry-mixing the powdered resin-conductive material particles and the carrier core material until the powdered particles adhere to the carrier core material by mechanical impaction and/or electrostatic attraction. Any suitable means may be employed for this purpose. Typical means for this purpose include combining the carrier core material and the powdered particles mixture by cascade roll-milling or tumbling, mulling, shaking, electrostatic powder cloud spraying, employing a fluidized bed, electrostatic disc processing, and an electrostatic curtain. Following application of the coating material powder particles to the carrier core material, the mixture of carrier material and powdered particles is heated to permit flow-out of the coating material powder particles over the surface of the carrier core material. After fusion of the coating particles to the carrier core particles, the coated carrier particles are cooled and classified to the desired particle size. The resultant coated carrier particles may have a fused coating over between about 15 percent and up to about 85 percent of their surface area. As will be appreciated, the concentration of coating material powder particles as well as the conditions of the heating step may be selected as to form a continuous film of the coating material on the surface of the carrier core material or leave selected areas of it uncoated. Where selected areas of the carrier core material remain uncoated or exposed, the carrier material will possess more strongly electrically conductive properties when the core material comprises a metal. Thus, when such partially coated carrier materials are provided, these carrier materials may possess both electrically insulating and electrically conductive properties. Due to the electrically conductive properties of these carrier materials, the carrier

materials provide desirably high triboelectric charging values when mixed with finely-divided toner particles.

Further, the dry, powdered resin-conductive material compositions and coating technique of this invention have been found to be especially effective in coating porous carrier cores to obtain coated carrier particles capable of generating high and useful triboelectric charging values to finely-divided toner particles and carrier particles and which possess significantly increased resistivities. In addition, when carrier particles are prepared by the powder coating technique of this invention, the majority of the coating material particles are fused to the carrier surface and thereby reduce the number of potential toner impaction sites on the carrier material.

Any suitable solid material having an average particle diameter of between about 30 microns and about 1,000 microns may be employed as the carrier core in this invention. However, it is preferred that the carrier core material be selected so that the coated core material acquire a charge having a polarity opposite to that of the toner particles when brought into close contact therewith so that the toner particles adhere to and surround the carrier particles. In employing the carrier particles of this invention, it is also preferred that the carrier particles be selected so that the toner particles acquire a positive charge and the carrier particles acquire a negative triboelectric charge. Thus, by proper selection of the developer materials in accordance with their triboelectric properties, the polarities of their charge when mixed are such that the electroscopic toner particles adhere to the surface of the carrier particles and also adhere to that portion of the electrostatic image-bearing surface having a greater attraction for the toner particles than the carrier particles.

In accordance with this invention, it is preferred that the carrier core material comprise low density, porous, magnetic or magnetically-attractable metal particles having a gritty, oxidized surface and a high surface area, i.e., a surface area which is at least about 200 cm^2/gram and up to about 1300 cm^2/gram of carrier material. Typical satisfactory carrier core materials include iron, steel, ferrite, magnetite, nickel and mixtures thereof. For ultimate use in an electrostatographic magnetic brush development system, it is preferred that the carrier core materials have an average particle size of between about 30 microns and about 250 microns. Excellent results have been obtained when the carrier core materials comprise porous, sponge iron or steel grit. The carrier core materials are generally produced by gas or water atomization processes or by reduction of suitable sized ore to yield sponge

powder particles. The powders produced have a gritty surface, are porous, and have high surface areas. By comparison, conventional carrier core materials usually have a high density and smooth surface characteristics.

Any suitable thermoplastic insulating resinous material which can be rendered in powdered form may be employed in this invention. Typical insulating coating materials include vinyl chloride-vinyl acetate copolymers, styrene-acrylate-organosilicon terpolymers, natural resins such as caoutchouc, carnauba, colophony, copal, dammar, jalap, storax; thermoplastic resins including the polyolefins such as chlorinated polyethylene, chlorosulfonated polyethylene, and copolymers and mixtures thereof; polyvinyls and polyvinylidenes such as polymethyl-styrene, polymethyl methacrylate, polyacrylonitrile, polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, polyvinyl chloride, polyvinyl pyridine, polyvinyl carbazole, polyvinyl ethers, and polyvinyl ketones; fluorocarbons such as polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride; and polychlorotrifluoroethylene; polyamides such as polycaprolactam and polyhexamethylene adipamide; polyesters such as polyethylene terephthalate; polyurethanes; polysulfides, thermosetting resins including phenolic resins such as phenol-formaldehyde, phenol-furfural and resorcinol formaldehyde; amino resins such as urea-formaldehyde and melamine-formaldehyde; polyester resins; and the like. Many of the foregoing and other typical carrier coating materials are described by L.E. Walkup in U.S. Patent No. 2,618,551; B.B. Jacknow et al in U.S. Patent No. 3,526,433; and R.J. Hagenbach et al in U.S. Patent Nos. 3,533,835 and 3,658,500. The preferred powdered coating materials of this invention are selected from fluorinated ethylene, fluorinated propylene and copolymers, mixtures, combinations or derivatives thereof such as fluorinated ethylene-propylene commercially available from E.I. Dupont Co., Wilmington, Delaware, under the tradename FEP; trichlorofluoroethylene, perfluoroalkoxy tetrafluoroethylene, polyvinylidene fluoride and the zinc and sodium salts of ionomer resins such as those containing carboxyl groups which are ionically bonded by partial neutralization with strong bases such as sodium hydroxide and zinc hydroxide to create ionic crosslinks in the intermolecular structure thereof and the like. Other preferred powdered coating materials are polyethylene, polypropylene, styrene and styrene copolymers or terpolymers, epoxy resins, polycarbonates, polysulfones, polyphenylene oxide, silicones, vinyl chloride and vinyl chloride copolymers, halogenated resins including homopolymers, copolymers, and terpolymers thereof. For use of the coated carrier particles in electrostato-

graphic development systems employing organic photoreceptors, it is preferred that the resinous coating material be of the type capable of providing negative triboelectric charging values to the carrier particles wherein the toner particles obtain a positive triboelectric charge for attraction of the toner particles to a negatively charged photoconductive surface.

Any suitable organic or inorganic electrically conductive material may be employed in this invention. Typical electrically conductive materials include metals, metal oxides, sulfides, halides, carbon, graphite, phthalocyanines, charge transfer complexes, quaternary ammonium compounds, and other conductive materials such as those described in U.S. Patent No. 3,533,835. Any suitable concentration of conductive material in the carrier coating may be employed. Typically, a loading of between about 3% to about 75% by weight, based on the weight of the carrier coating composition, i.e. the powdered particles, provides adequate electrical conductivity to the carrier particles. Coating compositions having a volume resistivity of less than about 10^{10} ohm-cm at 23°C are considered conductive. Some of the factors affecting the quantity of conductive material to be employed in the coating compositions include: the separation in the triboelectric series between the toner particles and the carrier material; the average diameter of the carrier particle; and the conductivity of the conductive material.

Any suitable finely-divided toner material may be employed with the carrier materials of this invention. Typical toner materials include, for example, gum copal, gum sandarac, rosin, asphaltum, phenol-formaldehyde resins, rosin-modified phenol-formaldehyde resins, methacrylate resins, polystyrene resins, polystyrene-butadiene resins, polyester resins, polyethylene resins, epoxy resins and copolymers and mixtures thereof. The particular type of toner material to be used depends to some extent upon the separation of the toner particles from the coated carrier particles in the triboelectric series. Patents describing typical electroscopic toner compositions include U.S. 2,659,670; 3,079,342; Reissue 25,136 and 2,788,288. Generally, the toner materials have an average particle diameter of between about 5 and 15 microns. Preferred toner resins include those containing a high content of styrene because they generate high triboelectric charging values and a greater degree of image definition is achieved when employed with the carrier materials of this invention. Generally speaking, satisfactory results are obtained when about 1 part by weight toner is used with about 10 to 200 parts

by weight of conductive powder coated carrier material.

Any suitable pigment or dye may be employed as the colorant for the toner particles. Toner colorants are well known and include, for example, carbon black, nigrosine dye, aniline blue, Calco Oil Blue, chrome yellow, ultramarine blue, duPont Oil Red, Quinoline Yellow, methylene blue chloride, phthalocyanine blue, Malachite Green Oxalate, lamp black, iron oxide, Rose Bengal and mixtures thereof. The pigment and/or dye should be present in the toner in a quantity sufficient to render it highly colored so that it will form a clearly visible image on a recording member. Thus, for example, where conventional xerographic copies of typed documents are desired, the toner may comprise a black pigment such as carbon black or a black dye such as Amaplast Black dye, available from National Aniline Products, Inc.. Preferably, the pigment is employed in an amount from about 3 percent to about 20 percent by weight, based on the total weight of the colored toner. If the toner colorant employed is a dye, substantially smaller quantities of colorant may be used.

The developer compositions of the instant invention may be employed to develop electrostatic latent images on any suitable electrostatic latent image-bearing surface including conventional photoconductive surfaces. Well known photoconductive materials include vitreous selenium, organic or inorganic photoconductors embedded in a non-photoconductive matrix, organic or inorganic photoconductors embedded in a photoconductive matrix, or the like. Representative patents in which photoconductive materials are disclosed include U.S. Patent No. 2,803,542 to Ullrich; U.S. Patent No. 2,970,906 to Bixby; U.S. Patent No. 3,121,006 to Middleton; U.S. Patent No. 3,121,007 to Middleton; and U.S. Patent No. 3,151,982 to Corrsin.

In the following examples, the relative triboelectric values generated by contact of carrier particles with toner particles is measured by means of a Faraday Cage. The device comprises a steel cylinder having a diameter of about 25 mm and a length of about 25 mm. A 400-mesh screen is positioned at each end of the cylinder. The cylinder is weighed, charged with about 0.5 gram mixture of carrier and toner particles and connected to ground through a capacitor and an electrometer connected in parallel. Dry compressed air is then blown through the steel cylinder to drive all the toner from the carrier. The charge on the capacitor is then read on the electrometer. Next, the chamber is reweighed to determine the weight loss. The resulting data is used to calculate the toner concentration and the charge in microcoulombs per

gram of toner. Since the triboelectric measurements are relative, the measurements should, for comparative purposes, be conducted under substantially identical conditions.

The following examples further define, describe and compare methods of preparing the carrier materials of the present invention and of utilizing them to develop electrostatic latent images. Parts and percentages are by weight unless otherwise indicated.

Example I

A control carrier material is prepared comprising about 97 parts of sponge iron carrier cores (available from Hoeganaes Corporation, Riverton, New Jersey, under the tradename ANCOR EH 80/150) having an average particle diameter of about 150 microns. A coating composition comprising about 10 percent solids of polyvinyl chloride and trifluorochloroethylene prepared from a material commercially available as FPC 461 from Firestone Plastics Company, Pottstown, PA., dissolved in methyl ethyl ketone is applied to the carrier cores as to provide them with a coating weight of about 3 percent. The coating composition is applied to the carrier cores via solution coating employing a vibratub (available from Vibraslide, Inc., Binghamton, New York).

About 97 parts by weight of the coated carrier particles are mixed with about 3 parts by weight of toner particles having an average diameter of about 12 microns. The composition of the toner particles comprises about 87 parts of a 65/35 styrene-n-butyl methacrylate copolymer, about 10 parts of carbon black and about 3 parts of nigrosine SSB. The mixture of carrier particles and toner particles is employed in a magnetic brush development testing fixture equipped with a photoreceptor charged to a negative polarity. The testing fixture is set as to provide a solid area density of about 1.3 to developed electrostatic latent images. It is found that this developer mixture is unsatisfactory in that the triboelectric charge generated on the toner material is about 14 microcoulombs per gram of toner, and the image background density is about 0.04 which is considerably above the acceptable level of 0.01. The electrical resistivity of the developer is about 3.8×10^{11} ohm-cms.

Example II

A carrier material is prepared comprising about 99 parts of sponge iron carrier cores as in Example I. The carrier cores are mixed for about 10

minutes with about 1.0 part of powdered polyvinyl chloride and trifluorochloroethylene prepared from a material commercially available as FPC 461 from Firestone Plastics Company, Pottstown, Pa.. The powdered coating material is attrited to an average particle diameter of less than about 44 microns. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of 177°C cooled to room temperature over a total process time of about 75 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is unsatisfactory in that the triboelectric charge generated on the toner material is about 16 microcoulombs per gram of toner, the developed image background density is about 0.03, and the image quality is unacceptable. The electrical resistivity of the developer is about 1.5×10^{11} ohm-cms.

Example III

A carrier material is prepared in the following manner. About 50 grams of polyvinylidene fluoride and tetrafluoroethylene copolymer commercially available as Kynar 7201 from Pennwalt Corporation, King of Prussia, Pa. is placed in a heating vessel and brought to a fluid state. About 3 grams of carbon black commercially available as Ketjenblack - EC from Armak Corporation, Chicago, Illinois is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then cooled and allowed to solidify into a solid mass. The solid mass is then converted to dry, powdered particles having an average particle size of less than about 44 microns by cryogenic grinding using liquid nitrogen to cool the pigmented polymer composition and steel shot having a diameter of about 1/8 inch as a grinding aid.

About 99 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 1 part of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 127°C and then cooled to room temperature over a total process time of about 15 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture

of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 25 microcoulombs per gram of toner material. The developed image background density is only about .008, and the image quality is excellent. The electrical resistivity of the developer is about 7.8 x 10^9 ohm-cms.

Example IV

A carrier material is prepared in the following manner. About 50 grams of polyvinylidene fluoride commercially available as Kynar 461 from Pennwalt Corporation, King of Prussia, Pa. is placed in a heating vessel and brought to a fluid state. About 5 grams of the carbon black of Example III is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then cooled and allowed to solidify into a solid mass. The solid mass is then converted to dry, powdered particles having an average particle size of less than about 44 microns by cryogenic grinding as in Example III.

About 98.5 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 1.5 parts of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 288°C and then cooled to room temperature over a total process time of about 90 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 28 microcoulombs per gram of toner material. The developed image background is only about .006, and the image quality is excellent. The electrical resistivity of the developer is about 5.4 x 10^9 ohm-cms.

Example V

A carrier material is prepared in the following manner. About 10 grams of polyvinylidene fluoride commercially available as Kynar 301 from

Pennwalt Corporation, King of Prussia, Pa. is placed in a polyethylene jar containing about 2 grams of carbon black and about 250 ml of propylene carbonate solvent. The mixture is placed on a Red Devil paint shaker to disperse the pigment. Steel shot, 3.2mm diameter, is present in the mixture as a milling aid. After about 10 minutes of mixing, the mixture is sieved to remove the steel shot and the dispersion is put into a beaker and heated with stirring to about 85°C to dissolve the resin. The temperature is maintained for about 15 minutes after which the dispersion is added to 500 ml of methanol with agitation at the rate of about 50 ml/min.. Fine sized polyvinylidene fluoride coated carbon black particles are obtained of about 3 to 10 microns after filtration and washing with water.

About 98.5 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 1.5 parts of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 277°C and then cooled to room temperature over a total process time of about 60 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 26 microcoulombs per gram of toner material. The developed image background density is only about .007, and the image quality is excellent. The electrical resistivity of the developer is about 1.3×10^9 ohm-cms.

Example VI

A carrier material is prepared in the following manner. About 50 grams of polyvinyl chloride and trifluorochloroethylene commercially available as FPC 461 from Firestone Plastics Company, Pottstown, Pa. is dissolved in about 300 mls of methyl ethyl ketone. About 4 grams of carbon black as in Example III is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then spray-dried to powdered particles having an average particle size of about 5 to 8 microns.

About 98.0 parts of the sponge iron carrier cores described in

Example I are mixed for about 10 minutes with about 2.0 parts of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 177°C and then cooled to room temperature over a total process time of about 60 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 19 microcoulombs per gram of toner material. The developed image background density is only about .007, and the image quality is excellent. The electrical resistivity of the developer is about 8.7×10^9 ohm-cms.

Example VII

A carrier material is prepared in the following manner. About 50 grams of polyvinylidene fluoride and tetrafluoroethylene copolymer commercially available as Kynar 7201 from Pennwalt Corporation, King of Prussia, Pa. is placed in a heating vessel and brought to a fluid state. About 3 grams of phthalocyanine is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then cooled and allowed to solidify into a solid mass. The solid mass is then converted to dry, powdered particles having an average particle size of less than about 44 microns by cryogenic grinding as in Example III.

About 99 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 1 part of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 127°C and then cooled to room temperature over a total process time of about 15 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is

higher than that obtained with the developer mixture of Example II, being about 23 microcoulombs per gram of toner material. The developed image background density is only about .006, and the image quality is excellent. The electrical resistivity of the developer is about 9.2×10^9 ohm-cms.

Example VIII

A carrier material is prepared in the following manner. About 50 grams of polyvinylidene fluoride commercially available as Kynar 201 from Pennwalt Corporation, King of Prussia, Pa. is placed in a heating vessel and brought to a fluid state. About 10 grams of aluminum commercially available as MD-796 from Alcan Metal Powders, Inc., of Elizabeth, New Jersey having an average particle size of less than about 45 microns is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then cooled and allowed to solidify into a solid mass. The solid mass is then converted to dry, powdered particles having an average particle size of less than about 50 microns by cryogenic grinding as in Example III.

About 98 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 2 parts of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 232°C and then cooled to room temperature over a total process time of about 70 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 32 microcoulombs per gram of toner material. The developed image background density is satisfactory and the image quality is excellent.

Example IX

A carrier material is prepared in the following manner. About 50 grams of polyvinylidene fluoride commercially available as Kynar 201 from Pennwalt Corporation, King of Prussia, Pa. is placed in a heating vessel and brought to a fluid state. About 10 grams of carbon black commercially

available as Vulcan XC-72 from Cabot Corporation, Boston, Mass. is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then cooled and allowed to solidify into a solid mass. The solid mass is then converted to dry, powdered particles having an average particle size of less than about 44 microns by cryogenic grinding as in Example III.

About 98 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 2 parts of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 232°C and then cooled to room temperature over a total process time of about 70 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 16 microcoulombs per gram of toner material. The developed image background density is satisfactory and the image quality is excellent.

Example X

A carrier material is prepared in the following manner. About 50 grams of vinyl chloride/vinyl acetate/maleic acid terpolymer commercially available as Vinylite VYNS from Union Carbide Corporation, New York, New York is placed in a heating vessel and brought to a fluid state. About 8 grams of carbon black as in Example IX is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then cooled and allowed to solidify into a solid mass. The solid mass is then converted to dry, powdered particles having an average particle size of less than about 44 microns by cryogenic grinding as in Example III.

About 97.5 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 2.5 parts of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about

135°C and then cooled to room temperature over a total process time of about 30 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 18 microcoulombs per gram of toner material. The developed image background density is satisfactory and the image quality is excellent. The electrical resistivity of the developer is about 7.6×10^9 ohm-cms.

Example XI

A carrier material is prepared in the following manner. About 50 grams of polyvinyl chloride and trifluorochloroethylene commercially available as FPC 461 from Firestone Plastics Company, Pottstown, Pa. is dissolved in about 300 mls of methyl ethyl ketone. About 4 grams of cetyl pyridinium chloride available from Hexcel Corporation, Lodi, New Jersey is added to the fluid resin composition and stirred therewith until a substantially uniform mixture is obtained. The mixture is then spray-dried to powdered particles having an average particle size of about 5 to 8 microns.

About 98 parts of the sponge iron carrier cores described in Example I is mixed for about 10 minutes with about 2 parts of the aforedescribed dry, powdered particles whereby the powdered coating composition electrostatically adheres to the carrier cores. The dry mixture is placed in a muffle furnace and heated to a maximum temperature of about 135°C and then cooled to room temperature over a total process time of about 30 minutes.

About 97 parts by weight of the coated carrier particles is mixed with about 3 parts by weight of toner particles as in Example I. The mixture of carrier and toner particles is employed as in Example I to develop an electrostatic latent image. It is found that this developer mixture is satisfactory in that the triboelectric charge generated on the toner material is higher than that obtained with the developer mixture of Example II, being about 18 microcoulombs per gram of toner material. The developed image background density is satisfactory and the image quality is excellent.

Although specific materials and conditions are set forth in the

foregoing examples, these are merely intended as illustrations of the present invention. Various other suitable thermoplastic toner resin components, additives, colorants, and development processes such as those listed above may be substituted for those in the examples with similar results. Other materials may also be added to the toner or carrier to sensitize, synergize or otherwise improve the fusing properties or other desirable properties of the system.

CLAIMS:-

1. A process for preparing coated carrier particles for electrostatographic developers characterised by preparing a fluid mixture of insulating resinous material and at least one electrically conductive agent, converting said fluid mixture to a solid state, comminuting said mixture in said solid state to dry, powdered particles, applying said powdered particles to the surface of carrier cores, and heating the resultant aggregation so that said powdered particles fuse to said carrier cores.

2. A process for preparing coated carrier particles in accordance with Claim 1 wherein the carrier core particles have an average diameter of between 30 and 1000 microns, the powdered particles have a particle size of between 1 and 100 microns, and the powdered particles comprise between 0.05 and 3 percent by weight of the coated carrier particles, and wherein the mixture is heated to a temperature of between 126°C and 345°C for between 15 and120 minutes.

3. A process for preparing carrier particles in accordance with Claim 1 or Claim 2 wherein said fluid mixture of resinous material and electrically conductive agent is obtained by melting said resinous material and adding said conductive agent thereto with mixing.

4. A process for preparing carrier particles in accordance with Claim 3 wherein said fluid mixture of resinous material and electrically conductive agent is cooled to a solid state and processed to form dry, powdered particles.

5. A process for preparing carrier particles in accordance with any one of Claims 1 to 4 wherein said powdered particles are applied to the surface of said carrier cores by dry-mixing said powdered particles and said carrier cores until said powdered particles adhere to said carrier cores by mechanical impaction and/or electrostatic attraction.

6. A process for preparing carrier particles in accordance with any one of Claims 1 to 5 wherein said carrier particles are provided with a fused coating of said insulating resinous material and said electrically conductive agent over between about 15 percent and about 85 percent of the surface area.

7. A process for preparing carrier particles in accordance with any one of Claims 1 to 6 wherein said carrier cores comprise low density, porous, magnetic or magnetically-attractable metal particles having a gritty, oxidised surface and a surface area of between 200 cm^2/gram and 1,300 cm^2/gram of carrier material.

8. A process for preparing carrier particles in accordance with any one of Claims 1 to 7 wherein said carrier cores are of iron, steel, ferrite, magnetite, nickel, or mixtures thereof.

9. A process for preparing carrier particles in accordance with any one of Claims 1 to 8 wherein said insulating resinous material is of fluorinated ethylene, fluorinated propylene, fluorinated ethylenepropylene, trichlorofluorethylene, perfluoroalkoxy tetrafluorethylene, polyvinylidene fluoride, polyvinyl chloride, trifluorochloroethylene, or derivatives thereof.

10. A process for preparing carrier particles in accordance with any one of Claims 1 to 9 wherein said electrically conductive agent is of carbon or graphite, or a metal, metal oxide, sulfide, or halide, or a phthalocyanine, a charge transfer complex, or a quaternary ammonium compound.

European Patent Office

EUROPEAN SEARCH REPORT

0020181

Application number
EP 80 30 1870

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	RESEARCH DISCLOSURE, no. 148, August 1976 Hampshire GB G.P. KASPER et al.: "A Process for coating carrier particles", pages 74-76, art. no. 14852 * Page 75, column 1, paragraphs 1-6; the examples * --	1,2,7, 8,9,10	G 03 G 9/10
	GB - A - 1 535 891 (PITNEY-BOWES) * The claims; page 1, line 56 - page 2, line 91 * --	1,2,7, 8,9	TECHNICAL FIELDS SEARCHED (Int.Cl. 3)
D	US - A - 3 533 835 (R.J. HAGENBACH) * The claims; the abstract; column 4, line 35 - column 8, line 29; column 8, line 72 - column 9, line 72 * --	1,2,7, 8,9,10	G 03 G 9/10 C 08 G 3/12 B 01 J 2/00
	RESEARCH DISCLOSURE, no. 128, December 1974 Hampshire GB A.E. FIELDS et al.: "Electrographic carrier particles", pages 15-16 art. no. 12844 * Page 15, column 2, paragraph 8, the examples * --	1,8,9, 10	
A	GB - A - 1 322 623 (ESSO) * Claims 5,8,9 * -- ./.	1	

CATEGORY OF CITED DOCUMENTS
X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	22-09-1980	VANHECKE

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 80 30 1870

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	GB - A - 1 437 536 (ATO CHIMIE) * The claims * ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)